

**Article with a Nanoscopic Coating of Precious/Semiprecious Metal
and Process for its Production**

The present invention relates to coated articles which contain a layer of copper or a copper alloy and a nanoscopic layer of precious metal and/or semiprecious metal, and which are particularly suitable as printed circuit boards or for the production of printed circuit boards.

Copper is one of the most widely used metallic materials of our time. Although copper is a semiprecious metal, this material is readily oxidizable, which often has an adverse effect on its use properties. This manifests itself not only visually but also has in particular practical technical disadvantages. Particular problems arise in the coating of printed circuit boards, which are then assembled in soldering processes, copper wires which are used as electrical conductors, or copper pipes. Finely divided

copper powders are practically impossible to produce and use without oxidation protection.

Copper is normally not, like iron and steel, provided with protective coatings which in the case of lacquers often have to be applied in several layers. Instead, as protection against copper corrosion, substances which form complexes with copper, such as for example imidazoles, benzimidazoles, benzotriazoles, thiourea and imidazole-2-thione, are predominantly used.

Such organic complexing agents are admittedly inexpensive and easy to process, however they display a number of disadvantages. Thus formulations with imidazoles or benzimidazoles often contain formic acid and sometimes other organic acids which smell unpleasant, are corrosive and have toxicological disadvantages. In addition, the thermal stability is low.

Therefore, in the production of printed circuit boards, for protection against corrosion copper is often coated with other metals such as for example gold, silver or tin, in order to preserve the solderability of the copper contacts and the copper-plated drill holes, which is otherwise lost in a very short time through oxidation.

An overview of common solderable end-surfaces and their technical, economic, ecological and toxicological advantages and disadvantages is to be found in "Alternative Technologies for Surface Finishing - Cleaner Technology for Printed Wired Board Manufacturers", EPA, Office of Pollution Prevention and Toxics, June 2001, EPA 744-R-01-001.

Metallic coatings are in general very suitable for printed circuit boards, however they also display a number of disadvantages. Coatings with gold (on an intermediate layer of nickel which is several micrometers thick) are expensive not only on account of the high price of gold, but in addition require special processes for the application of the gold layer. For example, gold cannot be chemically applied in so-called horizontal

systems but only in vertical systems, which results in additional high process costs. The so-called "black pad" phenomenon, which is a corrosion phenomenon, is known as a technical risk; likewise, so-called "microvoids" also occur.

The application of silver is difficult to reproduce, and the necessary system settings are difficult. In addition, silver-plated copper pads often tarnish e.g. due to sulphur compounds contained in the air. In addition, the mechanical strength and electric reliability of soldered joints on silver-plated copper pads is often greatly impaired by so-called "microvoids" which appear at the boundary surface.

A disadvantage common to all metallic coatings is that the deposition of the metallic layer requires a lot of time, which causes considerable apparatus and processing costs. On the other hand, organic coats are applied in a very much shorter time.

Tin is admittedly satisfactory from the technical and economic point of view, in particular when it is applied with the aid of an organic metal, such as for example in the ORMECON CSN process of Ormecon GmbH, however its deposition as a rule requires several minutes, which renders correspondingly large-sized systems necessary in order to ensure a high throughput.

A process is known from patent application DE 10 2004 030 388 with which the copper surfaces ("pads") to be soldered are coated with dispersions which contain essentially intrinsically electrically conductive polymers which equally protect against oxidation and preserve solderability.

This process is superior to conventional, purely organic coatings, so-called "OSPs" (= Organic Solderability Preservatives) in their resistance to aging, but still has some disadvantages. One of the disadvantages is that the coating is not visually detectable due to its thin layer thickness (less than 100 nm), which makes an initial quality check difficult. Moreover, its resistance to aging - although clearly improved compared with

conventional OSPs - is still much less than that of metallic coatings.

From EP 0 807 190 B1, a process for the production of metallized materials is known in which the material to be metallized is first coated with an intrinsically conductive polymer, the intrinsically conductive polymer is then activated by reduction and finally the metal is applied in a non-electrochemical manner in that the coated material is brought into contact with a solution of ions of the metal. The process is particularly suitable for the deposition of tin onto copper but also for the metallization of plastic surfaces.

In the patent application DE 10 2006 043 811.6 entitled "Article with a Coating of Electrically Conductive Polymer and Precious/Semiprecious Metal and Process for Production thereof" a coating is described which contains in particular 15 to 40% electrically conductive polymers (or organic metals) and 15 to 40% precious or semiprecious metals and is preferably 10 to 200 nm thick. This coating represents an enormous advance, but it transpired upon further investigation of the dispersion formulation and the coating parameters that the reproducibility when producing the layer can be improved still further.

The object of the invention is thus to provide a coating which can be applied as quickly and easily as organic coatings and also with very good reproducibility, but in the process at least attains the properties of metallic end-surfaces and avoids their disadvantages outlined above.

This object is achieved according to the invention by a coated article which has

- (i) at least one electrically non-conducting base layer,
- (ii) at least one layer of copper and/or a copper alloy, and

(iii) a nanoscopic layer 150 nm thick or less, which contains at least 80 wt.-%, relative to layer (iii), of at least one precious metal and/or semiprecious metal other than copper and which does not contain electrically conductive polymer,

wherein the copper or copper alloy layer (ii) is arranged between the layers (i) and (iii).

Further preferred embodiments of the present invention are disclosed in the dependent claims.

The (average) thickness of layer (iii) is thus 150 nm, e.g. 100 nm or less. It is determined by means of methods known in the state of the art, e.g. electrochemically or by means of EDX (Energy Dispersive X-Ray Analysis). In particular, there are no other materials between layers (i), (ii) and (iii).

The solution according to the invention is particularly surprising in so far as it was not to be expected, in the light of the state of the art, that such a thin layer would attain and exceed the property of known metallic end-layers which are in each case much thicker.

The layer thickness of layer (iii) is thus 150 nm or less, which contradicts the general expectation that a greater effect would be achieved with thicker layers.

According to the invention, the layer is at least 80% composed of the (semi)precious metal, but is not necessarily homogeneous, uniformly thick or dense. The details in this patent application relating to the thickness and composition in particular of layer (iii) according to the invention relate to the values as defined and measured above.

Layers according to the invention can be produced by various processes customary in nanotechnology. However, processes in which the (semi)precious metal is dissolved in a liquid medium

together with one or more organic complexing agent(s) or dispersed finely divided, and the metal precipitated out of this dispersion/solution, are particularly preferred. By finely divided is meant that the metal, i.e. the compound containing the metal, is present in the liquid medium in the form of particles of an average size smaller than 500 nm, or that the remaining constituents of the dispersion are present colloiddally dispersed in a particle size of < 500 nm.

It was now discovered according to the invention that, surprisingly, predominantly silver is precipitated starting from a concentration of 150 mg/l AgNO_3 or another precious or semiprecious metal salt suitable according to the invention in the presence of organic Cu complexing agents and with coating times of more than 60 seconds, preferably at least 90 seconds, and at temperatures above room temperature, e.g. above 25°C, preferably above 30°C.

Coatings produced in this way are remarkably resistant to various aging stresses. Thus the wetting angles are still below 60° even after 4 reflow steps. This resistance to aging is at least equivalent to that of a conventional silver layer which is normally at least 200 - 250 nm thick and with conventional "chemical-silver" or "immersion silver" processes (e.g. as marketed by the companies Cookson-Electronics or Enthone or MacDermid).

If the other named silver coating methods are used to apply e.g. 150 nm silver or less, these Ag layers produced according to processes known from the state of the art are scarcely age-resistant and quickly reduce the initially good solderability. The surface and the deposition are evidently favourably influenced by the organic Cu complexing agents.

Layer (iii) contains at least one precious metal which is selected in particular from the group Ag, Au, Pt, Pd, Rh, Ir, Ru, Os and Re, and/or a semiprecious metal which is selected from the group Ni, Ti, Cu, Sn and Bi. Layer (iii) can furthermore contain an organic component, in particular as a result of using

complexing agents during production, but no electrically conductive polymer, or mixtures thereof with other substances such as electrically non-conductive components.

Layer (iii) can also contain further additives, in particular surfactants, non-conductive polymers, viscosity modifiers, flow aids, drying aids, gloss improvers, flattening agents and mixtures thereof, preferably in a concentration of up to 20 wt.-% together with the conductive polymers or organic nanometals relative to the mass of layer (iii).

Preferred complexing agents are selected from the group consisting of nitrogen-containing organic compounds such as mono- or binuclear heterocycles, urea and its derivatives, chelating agents, polyamine carboxylic acid compounds or their salts and the like. Preferred complexing agents are imidazoles, benzimidazoles or comparable complexing agents, such as benzotriazoles, urea, thiourea, imidazole-2-thione, (sodium) ethylenediamine tetraacetate (EDTA), (K, Na) tartrates, ethylenediamine disuccinic acid, and mixtures thereof, which are characterized by a relatively good thermal stability.

Layer (iii) preferably contains more than 80% precious metal(s) or semiprecious metal(s), in particular more than 80 or e.g. 90 or 95%, relative to the mass of layer (iii).

Further constituents of layer (iii) are the above complexing agents and optionally further constituents which result from the layer-deposition process.

In accordance with a preferred embodiment, layer (iii) does not contain tin. According to another preferred embodiment, the at least one precious metal other than copper of layer (iii) is silver and the layer does not contain tin. Furthermore, it is preferred that none of the layers of the coated article of the present invention contains tin.

Furthermore, according to another preferred embodiment, the layers (i), (ii) and (iii) of the coated article consist of the materials as disclosed above and in the following description of the invention. For example, layer (iii) preferably consists of the at least one precious metal, in particular silver, wherein the content of said precious metal is at least 80 wt.-%, relative to layer (iii), for example, at least 90 or at least 95 wt.-%, and additives selected from electrically non-conductive components, viscosity, modifiers, flow aids, drying aids, gloss improvers, flattening agents and mixtures thereof as well as components resulting from the deposition-process as described herein, with the proviso that layer (iii) does not contain an intrinsically conductive polymer.

As base layer (i), all materials used in printed circuit board technology are suitable, in particular epoxides and epoxide composites, Teflon, cyanate esters, ceramics, cellulose and cellulose composites, such as for example cardboard, materials based on these substances and flexible base layers, for example based on polyimide. The base layer preferably has a layer thickness of 0.1 to 3 mm.

The copper layer or copper alloy layer (ii) preferably has a thickness of 5 to 210 μm , in particular 15 to 35 μm .

A further metal or alloy layer (iv) can be positioned between layer (ii) and layer (iii). Layer (iv) preferably contains silver, tin, gold, palladium or platinum. According to a preferred embodiment, layer (iv) contains mainly, i.e. more than 50 wt.-% relative to the mass of layer (iv), one or several of the said metals. The said metals can in particular be present as an alloy with copper. According to another preferred embodiment, layer (iv) consists exclusively of the said metals, either in pure form or in the form of an alloy. Layer (iv) preferably has a layer thickness of 10 to 800 nm. As well as the metal or the alloy, layer (iv) can contain organic components in a concentration of preferably 1 to 80 wt.-% relative to the total mass of layer (iv) (metal content 20 to 99 wt.-%). Preferred organic

components are conductive polymers or organic metals, or organic copper complexing agents such as thiourea or benzotriazoles.

The articles according to the invention are particularly suitable for the production of printed circuit boards, and the articles are preferably printed circuit boards which are also described as boards. These are thin plates used for the assembly of electrical components, with holes through which the leads of components are inserted for further soldering.

For the production of the coated articles according to the invention and in particular of printed circuit boards

- (1) a layer of copper or a copper-containing alloy is applied onto the surface of a base layer;
- (2) the layer produced in step (1) is optionally structured; and
- (3) a layer which contains at least one precious metal or semi-precious metal other than copper is applied to the optionally structured copper or copper alloy layer.

According to a preferred embodiment of the process, the copper or copper alloy layer (ii) is degreased and cleaned following step (1). For this the articles are preferably treated with normal commercial acidic cleaners. Cleaners based on sulphuric acid and citric acid, such as for example the cleaner ACL 7001 from Ormecon GmbH, are preferred. The articles are preferably left in the cleaning bath for about 2 minutes at 45°C and then washed with water.

In addition, it is preferable to pre-treat the copper or copper alloy layer (ii) oxidatively following step (1) or after the cleaning, for example by etching the surface with H_2O_2 or inorganic peroxides. Suitable etching solutions are commercially available, such as for example the hydrogen peroxide-containing solution Etch 7000 from Ormecon GmbH. The articles are pre-

ferably left in the etching solution for about 2 minutes at 30°C.

The layer produced in step (1) is preferably structured by lithographic or etching processes, whereby the conductor track structure is created.

The implementation of the individual steps of the above process is known per se to a person skilled in the art.

Layer (iii) is preferably applied to the article by treating it, after rinsing with water, with a dispersion/solution of an organic complexing agent in a dispersion/solvent which is liquid at a temperature of >25°C, for example by dipping the article in the dispersion or by applying the latter to the article. The precious metals or semiprecious metals are contained in particular as water-soluble ions in the dispersion medium in a concentration of ≥ 150 mg/l, e.g. in particular in a concentration of 180 mg/l, such as e.g. 200 mg/l, or in a range of greater than 150 mg/l to 250 mg/l, e.g. up to approx. 500 mg/l or up to approx. 1000 mg/l. Concentrations of up to a few g/l, e.g. up to 10 g/l, can also be suitable.

The article is preferably brought into contact with the dispersion for more than 60 seconds to 5 minutes, e.g. for 90 to 120 seconds, at $\geq 25^\circ\text{C}$. Contact is preferably established for 90 to 120 seconds at a temperature of 35°C to 45°C.

Additional components, such as electrically non-conductive polymers and additives, can be dissolved in the dispersion medium or also be present therein in colloidal form. As dispersion media, organic solvents, preferably organic solvents miscible with water, water and mixtures thereof are suitable. Preferred solvents miscible with water are alcohols, in particular alcohols with a boiling point of more than 100°C and preferably below 250°C. After the application of the dispersion onto the article, it is carefully dried and if necessary further dispersion is applied until the desired layer thickness is attained. The production

and use of dispersions suitable for coating is known from the state of the art, see for example EP 0 407 492 B1.

Water and aqueous solvents are preferred as dispersion medium. These are advantageous not only with regard to emissions and the non-wetting of the solder stop lacquer; it has also been found that water and aqueous solvents yield better results. This was surprising in that oxidation processes on copper proceed particularly rapidly in an aqueous environment. Solder stop lacquer is used to mask the areas of the printed circuit board which must not be wetted by the solder during the assembly process. The solder stop lacquer should not be wetted by the conductive polymer, since otherwise this would cause short circuits between the copper surfaces.

Preferably, dispersions which contain no formic acid are used, however, other acids and/or buffers can be contained in the dispersions.

For example, water-based compositions which contain imidazole, urea, thiourea or other Cu complexing agents, preferably a mixture of at least 2 of these complexing agents, can be considered as solutions suitable for coating.

The coated articles according to the invention are characterized in particular in that they can not only be soldered well even after prolonged storage, but are also solderable several times, i.e. can be used in multistage soldering processes, so-called reflow processes. In this respect, the properties of (much thicker) metallic coatings were attained and even exceeded.

In aging tests, the new coating is at least equivalent to all previously known end-surfaces. During aging the colour scarcely changes (from the original pale silver). It just turns somewhat darker. In reflow tests, no degradation in solderability was established even after 4 reflow steps.

Unlike conventional silver end-surfaces and nickel/gold, but also unlike conventional OSP surfaces, no microvoids are to be found.

Unlike conventional silver, there is no tarnishing and no reduction in the conductivity during storage in customary air atmosphere (printed circuit boards with a silver surface must be welded only shortly after they are manufactured in order to protect them against tarnishing and loss of solderability).

A summary of problems with silver end-surfaces and current approaches to their reduction can be found in an article by the silver end-surface manufacturer Enthone entitled: "Root Cause Analysis and Elimination of Immersion Silver Plating Defects on PWBs Through Process Optimization" by David Omerod, Yung Herng Yau, and Jo Wyszchenk, a paper given at the JPCA Show 2006 and to be found at: www.enthone.com/docs/JPCA2006.pdf.

A further presentation on microvoids entitled "Voids in Solder Joints" by Raiyo Aspandiar is to be found at www.smta.org/files/oregon_chapter_presentation0905.pdf, a paper given at the SMTA Northwest Chapter meeting on 21st September 2005.

The dispersions/solutions according to the invention as defined herein can also be used to protect copper powders against oxidation, wherein the copper powder particles have a size in the micrometer range, or sub-micrometer range, i.e. less than 1 μm .

The invention is further explained below by means of the figures and by non-limiting embodiment examples, wherein

Figure 1 shows a printed circuit board with a test design,
Figure 2 shows the heat profile in a reflow test.
Figure 3 shows an SEM image of a layer according to the invention, as outlined above

Examples

Example 1: Production of coated printed circuit boards

Printed circuit boards of epoxy resin composite were cleaned and degreased using a normal commercial cleaner based on sulphuric acid and citric acid (ACL 7001, Ormecon GmbH) in a cleaning bath for 2 minutes at 45°C. The printed circuit boards used had a test design (see Figure 1) which has been agreed with test institutes and printed circuit board manufacturers and is modelled on real printed circuit board structures. These boards enable the solderability to be measured and assessed. Next, the printed circuit boards were rinsed with tap-water at room temperature and then treated with an H₂O₂-containing etching solution (Etch 7000, Ormecon GmbH) for 2 minutes at 30°C. After etching, the plates were rinsed again with tap-water at room temperature and then coated with an aqueous formulation according to the invention which contained 400 mg/l AgNO₃, 100 mg/l polyvinyl alcohol, 50 mg/l complexing agent 2MZA from Shikokou (Japan), and 55 mg/l urea and 1.8 g/l citric acid. For this, the boards were immersed in the aqueous dispersion at 35°C for 90 seconds. After this, the printed circuit boards were dried at up to 100°C.

Example 2:

Printed circuit boards were coated analogously to Example 1, but the dispersion used contained no AgNO₃.

Example 3: Production of coated printed circuit boards (comparison)

Analogously to Examples 1 to 3, printed circuit boards were coated with normal commercial agents based on benzotriazole in accordance with the respective use instructions (Enthone / Cookson Electronics, USA, Example 4).

Example 4: Soldering angle measurement

The boards were subjected to a reflow test. The board is subjected to a heat profile as shown in Figure 2 in a commercial reflow oven which is used for modern lead-free soldering methods. The reflow cycles serve to simulate repeated soldering operations. The soldering angle is then measured by means of a soldering balance.

The results of the soldering angle measurements are shown in the table below.

Table: Results of the soldering angle measurement

Test	Reflow steps	Soldering angle WA (°)	WA after aging 155°/4h
Example 1	0	25-30	30-35
	1	30-35	35-40
	2	35-40	40-50
	3	40-50	40-50
	4	40-50	50-60
Example 2 (comparison test)	0	40	> 90
	1	50	> 90
	2	>60	> 90
	3	> 90	> 90
	4	> 90	> 90
Example 3: Comparison test Conventional OSP	0	25-30	>90
	1	40-50	>90
	2	65-70	>90
	3	>90	>90
	4		>90

It can be seen that the coating according to the invention has small soldering angles even after repeated reflow cycles and smaller angles than comparison surfaces. This indicates better solderability.

Claims

1. Coated article, which has
 - (i) at least one electrically non-conducting base layer,
 - (ii) at least one layer of copper and/or a copper alloy, and
 - (iii) a nanoscopic layer having a thickness of 150 nm or less, which contains at least 80 wt.-%, relative to layer (iii), of at least one precious metal and/or semiprecious metal other than copper and which does not contain electrically conductive polymer,wherein the copper or copper alloy layer (ii) is arranged between layers (i) and (iii).
2. Coated article according to claim 1, in which the precious metal is selected from the group consisting of Ag, Au, Pd, Pt, Rh, Ir, Ru, Os, Re, preferably Ag, Au, in particular Ag.
3. Coated article according to claim 1 or 2, in which the semiprecious metal is selected from the group consisting of Ni, Ti, Cu, Sn, Bi, in particular Ni, Ti.
4. Coated article according to one of the previous claims, in which layer (iii) has an average layer thickness of 2 nm to 100 nm.
5. Coated article according to one of the previous claims, in which layer (iii) also contains at least one organic constituent derived from organic complexing agents.
6. Coated article according to one of the previous claims, in which the organic complexing agent is one which is capable of complexing copper.

7. Coated article according to one of the previous claims, in which layer (iii) contains at least one electrically non-conducting component.
8. Coated article according to one of the previous claims, in which layer (iii) contains more than 90% (semi)precious metal other than copper, relative to the mass of layer (iii).
9. Coated article according to claim 7 or 8, in which the electrically non-conducting component is a polymer.
10. Coated article according to claim 5, in which the complexing agent is selected from benzimidazoles, imidazoles, benzotriazoles, thiourea, imidazole-2-thiones, urea, thiourea, (sodium) ethylenediamine tetraacetate (EDTA) (Ka, Na) tartrates, ethylenediamine disuccinic acid, derivatives and mixtures thereof.
11. Coated article according to one of the previous claims, in which the base layer (i) contains epoxide, epoxide composite, Teflon, cyanate ester, ceramic, cellulose, cellulose composite, cardboard and/or polyimide.
12. Coated article according to one of the previous claims, in which the base layer (i) has a layer thickness of 0.1 to 3 mm.
13. Coated article according to one of the previous claims, in which layer (ii) has a layer thickness of 5 to 210 μ m.
14. Coated article according to one of the previous claims, which contains a further metal or alloy layer (iv) which is positioned between layer (ii) and layer (iii).
15. Coated article according to claim 14, in which layer (iv) contains silver, tin, gold, palladium or platinum.

16. Coated article according to claim 14 or 15, in which layer (iv) has a layer thickness of 10 to 800 nm.
17. Coated article according to one of the previous claims in the form of a printed circuit board.
18. Process for the production of a coated article according to one of the previous claims, in which
 - (1) a layer of copper or a copper-containing alloy is applied onto the surface of a base layer,
 - (2) the layer produced in step (1) is optionally structured; and
 - (3) a layer which contains at least one precious metal and/or semiprecious metal or a mixture thereof other than copper is applied, using at least one organic complexing agent, to the optionally structured copper or copper alloy layer.
19. Process according to claim 18, in which the precious metal is selected from the group consisting of Ag, Au, Pd, Pt, Rh, Ir, Ru, Os, Re, preferably Ag, Au, in particular Ag.
20. Process according to claim 18 or 19, in which the semiprecious metal is selected from the group consisting of Ni, Ti, Cu, Sn, Bi, in particular Ni, Ti.
21. Process according to one of the previous claims 18 to 20, in which the at least one organic complexing agent is selected from the group consisting of benzimidazoles, imidazoles, benzotriazoles, thiourea, imidazole-2-thiones, urea, thiourea, (sodium) ethylenediamine tetraacetate (EDTA), (K_a, Na) tartrates, ethylenediamine disuccinic acid, derivatives and mixtures thereof.

22. Process according to one of the previous claims 18 to 21, in which the at least one semiprecious/precious metal is dissolved or dispersed finely divided and the metal is precipitated from this dispersion/solution.
23. Process according to one of claims 18 to 22, in which the copper or copper alloy layer (ii) is subjected to cleaning following step (1).
24. Process according to one of claims 18 to 22, in which the copper or copper alloy layer (ii) is subjected to an oxidative pre-treatment following step (1) or after the cleaning.
25. Process according to one of claims 18 to 24, in which a solution or a finely divided dispersion is used which contains a medium liquid at room temperature, at least one organic complexing agent and at least one precious metal and/or semiprecious metal in a concentration of more than 150 mg/l.
26. Process according to claim 25, in which the solution or dispersion contains at least one further component which is selected from electrically non-conductive components, viscosity modifiers, flow aids, drying aids, gloss improvers, flatting agents and mixtures thereof.
27. Process according to claim 25 or 26, in which the dispersion medium contains water, an organic solvent miscible with water or a mixture thereof.
28. Use of a dispersion or solution according to one of the previous claims 25 to 27 to protect copper powders, wherein the copper powder particles have a size in the micrometer range or sub-micrometer range, before oxidation.

Abstract

The invention relates to a coated article which contains (i) at least one electrically non-conducting base layer, (ii) at least one layer of copper and/or a copper alloy, and (iii) a nanoscopic layer 150 nm thick or less, which contains at least 80 wt.-%, relative to layer (iii), at least one precious metal and/or semiprecious metal other than copper, wherein the copper or copper alloy layer (ii) is arranged between layers (i) and (iii). The invention further relates to a process for the production of such a coated article.

Figure 1

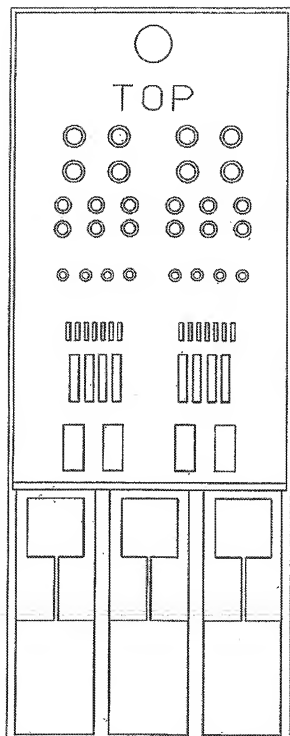


Figure 2

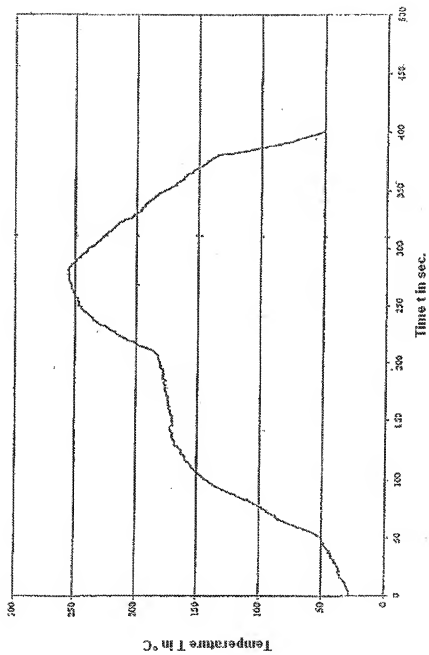


Figure 3

